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Elastic Interaction of Two Atoms Adsorbed on a Solid Surface ⁺

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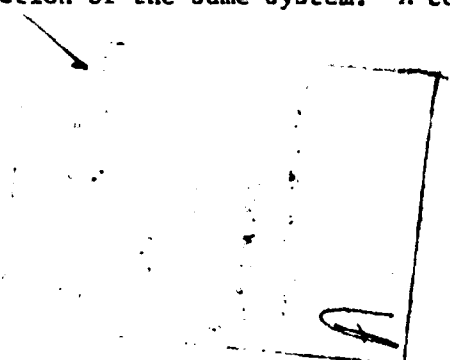
Abstract

The long-range interaction of two adsorbed atoms mediated by the elastic distortion of the substrate is calculated classically for an elastically isotropic substrate. For identical atoms, the interaction is repulsive; for different atoms, it can be repulsive or attractive. It varies as ρ^{-3} with the distance ρ between the two adsorbed atoms. This is the same spatial dependence as for the dipole-dipole interaction between two adsorbed atoms. For two xenon atoms adsorbed on silver, the elastic interaction is about one order of magnitude smaller than the dipole-dipole interaction. The interaction energy is inversely proportional to the shear modulus of the substrate, so that it may become quite large near a distortive phase transition.

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Atoms adsorbed on the surface of a solid interact with each other directly as well as indirectly through the substrate. The dipole-dipole interaction between two adatoms on a metal substrate varies as ρ^{-3} with the distance ρ between them⁽¹⁾. The oscillatory interaction mediated by the conduction electrons in a metal was discussed by Grimley,^{(2),(3)} Einstein and Schrieffer⁽⁴⁾, and appears to have been experimentally observed by Tsong.⁽⁵⁾ We shall show in a forthcoming paper that this interaction decays more rapidly than ρ^{-3} . In the present paper we investigate the classical long-range interaction between two adatoms mediated by the elastic distortion of the substrate. Different aspects of the lattice-mediated interaction has been studied by Schick and Campbell,⁽⁶⁾ and by Cunningham et al.^{(7),(8)}. We shall discuss these in Sec. VI.

An expression for the strain of a solid acted on by external forces, due to the presence of an adsorbed atom, is derived in Sec. II, and an expression for the interaction energy between two adatoms is obtained in Sec. III. A rough estimate for the magnitude of this interaction is also given. Because of the reduced symmetry near a surface, a quantum mechanical calculation of this interaction is rather complicated and was not carried out. However, in the appendix, we show that in the case of two impurities in an infinite lattice, quantum mechanical and classical calculations give the same asymptotic interaction energy, and we expect that the same is true in the vicinity of a surface. We show, in Sec. IV, that the interaction energy between identical adatoms is repulsive. Also the interaction between any two physisorbed atoms, identical or not, is shown to be always repulsive. In Sec. V, we calculate the elastic interaction energy between two xenon atoms adsorbed on the surface of silver, and compare it with the dipole-dipole interaction of the same system. A concluding discussion is given in Sec. VI.



II Strain of the Lattice due to an Adatom

Consider an atom on the surface of a solid occupying the space $z \leq 0$. The adatom exerts forces \underline{F}_i on the substrate atoms at positions $\underline{r}_i = (x_i, y_i, z_i)$. The strain of the lattice at a point \underline{r} far away from the adatom, where the direct interaction between the adatom and the substrate atoms is negligible, is calculated as follows: We treat the substrate as an elastically isotropic half-space with Lamé moduli μ and λ , and subject to external forces \underline{F}_i acting at the points \underline{r}_i . The displacement $\underline{u} = (u, v, w)$ at $\underline{r} = (x, y, z)$ in a half-space $z \leq 0$ acted on by an external force $\underline{F} = (F_x, F_y, F_z)$ at the origin is given by⁽⁹⁾

$$\begin{aligned} u = & \frac{F_x}{4\pi\mu} \left[\frac{1}{r} + \frac{x^2}{r^3} + \frac{\mu}{\mu+\lambda} \left(\frac{1}{r-z} - \frac{x^2}{r(r-z)^2} \right) \right] \\ & + \frac{F_y}{4\pi\mu} \left[\frac{xy}{r^3} - \frac{\mu}{\mu+\lambda} \frac{xy}{r(r-z)^2} \right] \\ & + \frac{F_z}{4\pi\mu} \left[\frac{xz}{r^3} - \frac{\mu}{\mu+\lambda} \frac{x}{r(r-z)} \right] , \end{aligned} \quad (2.1)$$

with a similar expression for v . The z -component of the displacement is not needed here. We now sum the displacements due to the forces \underline{F}_i exerted by the adatom at the positions \underline{r}_i . The forces are assumed to be central. For a system with 3-fold or 4-fold symmetry about the axis through the adsorbate normal to the substrate surface, and taking into account that the forces on the substrate atoms must add up to zero, the displacement at a point near the surface far from the adatom is found to be

$$\left. \begin{aligned} u = & \frac{2\mu+\lambda}{8\pi\mu(\mu+\lambda)} \left(\sum_i \underline{F}_i \cdot \underline{r}_i \right) \frac{x}{r^3} \\ v = & \frac{2\mu+\lambda}{8\pi\mu(\mu+\lambda)} \left(\sum_i \underline{F}_i \cdot \underline{r}_i \right) \frac{y}{r^3} \end{aligned} \right\} \quad (2.2)$$

with $\underline{\rho}_i = (x_i, y_i, 0)$.

III Interaction Energy of Two Adatoms

The energy of the system consisting of the lattice and an adatom relative to that of the unstrained lattice is

$$E = -\frac{1}{2} \sum_i \underline{F}_i \cdot \underline{u}_i \quad (3.1)$$

For two adatoms, (1) and (2) at \underline{r}_1 and \underline{r}_2 respectively, (see Fig 1), the elastic energy is

$$E = -\frac{1}{2} \sum_i (\underline{F}_i^{(1)} + \underline{F}_i^{(2)}) \cdot (\underline{u}_i^{(1)} + \underline{u}_i^{(2)}) \quad (3.2)$$

where $\underline{F}_i^{(\alpha)}$ is the force on the substrate atom i exerted by adatom α and $\underline{u}_i^{(\alpha)}$ is the displacement of atom i due to $\underline{F}_i^{(\alpha)}$

The interaction energy is given by

$$\begin{aligned} E_{\text{int}} &= -\frac{1}{2} \sum_i (\underline{F}_i^{(1)} \cdot \underline{u}_i^{(2)} + \underline{F}_i^{(2)} \cdot \underline{u}_i^{(1)}) \\ &= \frac{1-\sigma}{8\pi\mu} \left(\sum_i \underline{F}_i^{(1)} \cdot (\underline{\rho}_i - \underline{\rho}_1) \right) \left(\sum_j \underline{F}_j^{(2)} \cdot (\underline{\rho}_j - \underline{\rho}_2) \right) |\underline{\rho}_1 - \underline{\rho}_2|^{-3} \end{aligned} \quad (3.3)$$

where $\underline{\rho}_\alpha = (x_\alpha, y_\alpha, 0)$, and $\underline{\rho}_{12} = \underline{\rho}_2 - \underline{\rho}_1$

and $\sigma = \frac{\lambda}{2(\mu + \lambda)}$ is the Poisson ratio of the substrate.

The interaction energy can also be expressed in terms of the strains produced in the substrate by the adatoms. We introduce the two-dimensional dilatation (due to adatom α)

$$\theta^\alpha = \frac{\partial u^{(\alpha)}}{\partial x} + \frac{\partial v^{(\alpha)}}{\partial y} = -\frac{1-\sigma}{4\pi\mu} \left(\sum_i \underline{F}_i^{(\alpha)} \cdot (\underline{\rho}_i - \underline{\rho}_\alpha) \right) |\underline{\rho} - \underline{\rho}_\alpha|^{-3} \quad (3.4)$$

The quantity $\Theta^{(\alpha)} |\underline{\rho} - \underline{\rho}_\alpha|^3$ is a constant, independent of position. Substituting this into (3.3) we obtain

$$E_{\text{int}} = \frac{2\pi\mu}{1-\sigma} \left(\Theta^{(1)} |\underline{\rho} - \underline{\rho}_1|^3 \right) \left(\Theta^{(2)} |\underline{\rho} - \underline{\rho}_2|^3 \right) \rho_{12}^{-3} \quad (3.5)$$

To obtain an order of magnitude estimate for the strength of the interaction, let us assume that at $|\underline{\rho} - \underline{\rho}_\alpha| = 5 \text{ a.u.}$ (which corresponds roughly to the position of the substrate atom nearest to the adatom) $\Theta^{(\alpha)} = 0.1$. For most metals $\sigma \approx \frac{1}{2}$ and $\mu \approx 10^{-3} \text{ a.u.}$ This gives, for two adatoms 10 a.u. apart, an interaction energy of about 0.05 eV.

IV The Sign of the Interaction Energy

The interaction between two adatoms may be repulsive or attractive, depending on the relative signs of the sums in parentheses in (3.3), or of $\Theta^{(1)}$ and $\Theta^{(2)}$ in (3.4).

For identical adatoms, they have the same sign and hence the interaction is repulsive.

We shall now show that it is also repulsive between physisorbed atoms, where the repulsive potential between the adatom and the substrate atoms is of shorter range than the attractive potential. Since the adatom is in equilibrium we have, for forces in the z-direction

$$\sum_i (F_i^{(r)} - F_i^{(a)}) \frac{z_i}{R_i} = 0 \quad (4.1)$$

where $F_i^{(r)}$ and $F_i^{(a)}$ are the magnitudes of the repulsive and attractive parts of the force \underline{F}_i respectively and R_i is the distance between the adatom and the substrate atom at site i , with z_i the z-component (see Fig 2).

Since the repulsive force is of shorter range, we have $F_n^{(r)} \geq F_n^{(a)}$ for sites n within a certain distance R_0 from the adatom and $F_m^{(r)} < F_m^{(a)}$ for sites m farther away

(4.1) can be written as

$$\sum_n (F_n^{(r)} - F_n^{(a)}) \frac{z_n}{R_n} = \sum_m (F_m^{(a)} - F_m^{(r)}) \frac{z_m}{R_m} \quad (4.2)$$

with each term on either side of the equality positive.

Now, for each layer of substrate atoms, with constant z_0

$$\sum_n (F_n^{(r)} - F_n^{(a)}) \frac{z_0}{R_n} < \frac{z_0}{R_0} \sum_n (F_n^{(r)} - F_n^{(a)})$$

and

$$\sum_m (F_m^{(a)} - F_m^{(r)}) \frac{z_0}{R_m} > \frac{z_0}{R_0} \sum_m (F_m^{(a)} - F_m^{(r)})$$

so that

$$\sum_n (F_n^{(r)} - F_n^{(a)}) > \sum_m (F_m^{(a)} - F_m^{(r)}) \quad (4.3)$$

We now examine the sum in (3.3),

$$\begin{aligned} \sum_i (F_i \cdot \rho_i) &= \sum_i (F_i^{(r)} - F_i^{(a)}) \frac{\rho_i^2}{R_i} \\ &= \sum_n (F_n^{(r)} - F_n^{(a)}) \frac{\rho_n^2}{R_n} - \sum_m (F_m^{(a)} - F_m^{(r)}) \frac{\rho_m^2}{R_m} \end{aligned}$$

$$< \frac{\rho_0^2}{R_0} \left[\sum_n (F_n^{(r)} - F_n^{(a)}) - \sum_m (F_m^{(a)} - F_m^{(r)}) \right] < 0 \quad (4.4)$$

Thus (4.4) is always negative, i.e., the interaction energy (3.3) is repulsive between physisorbed atoms.

V Application to Xenon Atoms Adsorbed on Silver Surface

As a specific example, we consider the adsorption of noble gas atoms on the (111) face of a fcc crystal, with the adatoms at centered sites (symmetrical between three surface atoms). The attractive potential is taken to be of the form $\sum_i |R - R_i|^{-6}$ and the repulsive part taken to be some short-range potential. We make the approximation that silver is an isotropic material.

If we consider only the attractive interaction between the adatom and the three nearest substrate atoms, we have

$$\sum_i (F_i \cdot \rho_i) = \sqrt{3} F_0 a$$

$$\text{with } F_0 = - \frac{6\gamma a}{\sqrt{3} R_0^8}$$

where a = distance between two nearest neighbor substrate atoms

R_0 = distance between the adatom and one of the nearest substrate atoms

F_0 = component parallel to the substrate surface of the attractive force between the adatom and one of the nearest substrate atoms.

Including the repulsive interaction and the interaction between the adatom and other substrate atoms in the sum, we obtain the value

$$\sum_i (F_i \cdot \rho_i) = \alpha \sqrt{3} F_0 a \quad (5.1)$$

where α is a dimensionless number which depends on the distance of the adatom from the substrate surface.

The interaction energy is thus

$$E_{\text{int}} = \frac{9a^4}{2\pi\mu} (1-\sigma) \left(\frac{\alpha\gamma}{R_0^8} \right) \rho_{12}^{-3}$$

$$= Aa^4 \frac{1-\sigma}{2\pi\mu} \left(\frac{C}{Z(Z-Z_0)^4} \right)^2 \rho_{12}^{-3} \quad (5.2)$$

where the attractive potential is now written in the form⁽¹⁰⁾ (see Fig 3)

$$-\sum_i \frac{\gamma}{|\underline{R}-\underline{R}_i|^6} = - \frac{C}{(Z-Z_0)^3} \quad (5.3)$$

with Z the position of the adatom relative to the first layer of substrate atoms

Z_0 the position of the "reference plane"

C the van der Waals coefficient

and A a dimensionless constant depending on α

For xenon adsorbed on silver, we have, in atomic units, $C = 0.813$, $Z = 6.85$, $Z-Z_0 = 4.10$ ⁽¹⁰⁾, $a = 5.47$, $\mu = 10^{-3}$, $\sigma = 0.6$ and $A = 0.65$. This gives, for xenon atoms separated by a distance of 10 a.u. (which corresponds to monolayer coverage), an interaction energy of roughly 10^{-4} eV. The interaction is repulsive and varies as ρ^{-3} with the distance ρ between the two adsorbed atoms. This is the same spatial dependence as for the dipole-dipole interaction of the two adatoms, which is⁽¹⁾

$$E_{\text{dip-dip}} = 2\mu_1\mu_2 \rho^{-3}$$

where μ_1 and μ_2 are the dipole moments of the adatoms 1 and 2 .
 For xenon atoms adsorbed on silver at monolayer coverage, $\mu = 0.2$ debye⁽¹¹⁾,
 giving $E_{\text{dip-dip}} = 10^{-3}$ eV.

VI Conclusion

The elastic interaction energy of two adatoms is repulsive for identical atoms and also for any two physisorbed atoms. For arbitrary adatoms, the interaction may be attractive or repulsive. The spatial dependence is ρ^{-3} , which is the same as for the dipole-dipole interaction. For xenon adsorbed on silver, the elastic interaction is roughly one order of magnitude smaller than the dipole-dipole interaction energy, and the same is true for xenon on other noble metals. For chemisorbed atoms, the interaction energy between pairs of adatoms at monolayer coverage is roughly 0.01 to 0.1 eV. We note, from (3.3) that the interaction energy is inversely proportional to the shear modulus μ of the substrate, so that it may become quite large near a distortive phase transition.

Finally, we would like to compare our work with two previous calculations of the interaction energy between adsorbed atoms mediated by the substrate lattice.

Schick and Campbell⁽⁶⁾ calculated the phonon-mediated interaction energy of non-localized helium atoms adsorbed on argon-plated copper. They treated the adatoms as Bloch waves, with two-dimensional quasimomentum parallel to the surface, in contrast to the present calculation, which deals with atoms localized at definite sites. Cunningham et al. calculated the total phonon zero point energy of a simple cubic lattice with two adatoms localized at two sites a distance ρ apart. They obtained a weak attractive interaction behaving as ρ^{-7} at large distances. This interaction may be regarded as the leading quantum correction to the classical distortive interaction calculated in the present paper. (In the particular oversimplified model of Cunningham et al. the classical distortion is exactly zero). For adatoms at nearest neighbor sites with all masses and direct interactions taken as comparable they find for their indirect interaction

$$E_{\text{zero-point}} \sim -10^{-4} \hbar \omega_L ,$$

where ω_L is a characteristic frequency of the lattice. With the same assumptions the classical distortion energy calculated in the present paper is

$$E_{\text{distortion}} \sim 10^{-2} K a_0^2$$

where K is an interatomic force constant and a_0 is the lattice constant.

Typically, then,

$$E_{\text{zero-point}}/E_{\text{distortion}} \sim 10^{-3} \text{ or } 10^{-4} \text{ (nearest-neighbors)}$$

Because of the more rapid fall-off of the zero-point interaction compared to the distortive interaction, the ratio becomes even smaller, for more widely separated adatoms.

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APPENDIX: Elastic Interaction Energy of Two Defects in an Infinite Lattice

We calculate, both quantum mechanically and classically, the elastic energy of a large isotropic crystal of volume Ω with two defects in the interior, at \underline{r}_1 and \underline{r}_2 , which exert forces (per unit volume) $\underline{F}^{(1)}$ and $\underline{F}^{(2)}$ on the atom at site \underline{l} and shall verify that the results are identical for large separations.

To calculate the energy quantum mechanically, we write the perturbing potential as

$$\delta V = -\frac{\Omega}{N} \sum_{\underline{l}} (\underline{F}_{\underline{l}}^{(1)} + \underline{F}_{\underline{l}}^{(2)}) \cdot \underline{u}_{\underline{l}} \quad (\text{A.1})$$

and express the displacement vector $\underline{u}_{\underline{l}}$ in terms of phonon operators

$$\underline{u}_{\underline{l}} = \sum_{\underline{q}, j} \left(\frac{\hbar}{2NM\omega_j(\underline{q})} \right)^{1/2} \left(a_j(\underline{q}) + a_j^\dagger(-\underline{q}) \right) e^{i\underline{q} \cdot \underline{l}} \underline{\sigma}_j(\underline{q}) \quad (\text{A.2})$$

with wavevector \underline{q} , polarization index j and polarization vector $\underline{\sigma}_j(\underline{q})$.

We express the force $\underline{F}_{\underline{l}}$ in terms of the polarization vectors

$$\underline{F}_{\underline{l}} = \underline{F}_{\underline{l}}^{(1)} + \underline{F}_{\underline{l}}^{(2)} = \sum_{\underline{q}, j} \left\{ F_j^{(1)}(\underline{q}) e^{i\underline{q} \cdot (\underline{l} - \underline{r}_1)} \underline{\sigma}_j(\underline{q}) + F_j^{(2)}(\underline{q}) e^{i\underline{q} \cdot (\underline{l} - \underline{r}_2)} \underline{\sigma}_j(\underline{q}) \right\} \quad (\text{A.3})$$

The energy of the system relative to its ground state is, by second-order perturbation theory,

$$E = \sum_{\underline{q}, j} \frac{|\langle 0 | \delta V | \underline{q}, j \rangle|^2}{-\hbar\omega_j} = -\frac{\Omega}{d} \left\{ \frac{1}{2} \sum_{\underline{q}, j} \frac{|F_j^{(1)}(\underline{q})|^2 + |F_j^{(2)}(\underline{q})|^2}{\omega_j^2(\underline{q})} + \sum_{\underline{q}, j} \frac{F_j^{(1)}(\underline{q}) F_j^{(2)}(-\underline{q})}{\omega_j^2(\underline{q})} \cos(\underline{q} \cdot \underline{R}) \right\} \quad (\text{A.4})$$

Here d is the density of the crystal, and $\underline{R} = \underline{r}_2 - \underline{r}_1$. The second term on the right side of (A.4) represents the elastic interaction energy of

the defects:

$$E_{\text{int}} = - \frac{\Omega}{d} \iint \sum_j \frac{F_j^{(1)}(\underline{q}) F_j^{(2)}(-\underline{q})}{\omega_j^2(\underline{q})} \cos(\underline{q} \cdot \underline{R}) \} d^3 \underline{q} \quad (\text{A.5})$$

The classical elastic energy of the system is given by

$$E^{\text{cl}} = - \int \underline{F}(\underline{r}) \cdot \underline{u}(\underline{r}) d^3 \underline{r} \quad (\text{A.6})$$

with the displacement $\underline{u}(\underline{r})$ determined by the equation

$$\mu \nabla^2 \underline{u} + (\mu + \lambda) \nabla(\nabla \cdot \underline{u}) + \underline{F} = 0 \quad (\text{A.7})$$

Taking the force $\underline{F}(\underline{r})$ to be of the form (A.3) but with the label \underline{l} replaced by the continuous variable \underline{r} , the solution for (A.7) is found to be

$$\underline{u}(\underline{r}) = \begin{pmatrix} u \\ v \\ w \end{pmatrix} = \sum_{\alpha} \sum_{\underline{q}} \begin{pmatrix} \frac{F_L^{\alpha}}{2\mu+\lambda} \sin\theta \cos\varphi + \frac{F_{T1}^{\alpha}}{\mu} \cos\theta \cos\varphi - \frac{F_{T2}^{\alpha}}{\mu} \sin\varphi \\ \frac{F_L^{\alpha}}{2\mu+\lambda} \sin\theta \sin\varphi + \frac{F_{T1}^{\alpha}}{\mu} \cos\theta \sin\varphi + \frac{F_{T2}^{\alpha}}{\mu} \cos\varphi \\ \frac{F_L^{\alpha}}{2\mu+\lambda} \cos\theta - \frac{F_{T1}^{\alpha}}{\mu} \sin\theta \end{pmatrix} \frac{e^{i\underline{q} \cdot (\underline{r} - \underline{r}_{\alpha})}}{q^2} \quad (\text{A.8})$$

with θ and φ the polar and azimuthal angles of \underline{q}

$\alpha = 1$ or 2 denoting the defects 1 and 2

and $j = L, T_1$ or T_2 referring to the longitudinal or transverse components.

The elastic energy is thus

$$E = - \frac{1}{2} \int \underline{F} \cdot \underline{u} d^3 \underline{r}$$

$$= - \frac{\Omega}{2} \sum_{\underline{q}} \frac{1}{q^2} \left(\frac{2|F_T^{(1)}(\underline{q})|^2 + 2|F_T^{(2)}(\underline{q})|^2}{\mu} + \frac{|F_L^{(1)}(\underline{q})|^2 + |F_L^{(2)}(\underline{q})|^2}{2\mu+\lambda} \right) -$$

$$\Omega \sum_{\underline{q}} \frac{\cos(\underline{q} \cdot \underline{R})}{q^2} \left(\frac{2F_T^{(1)}(\underline{q})F_T^{(2)}(-\underline{q})}{u} + \frac{F_L^{(1)}(\underline{q})F_L^{(2)}(-\underline{q})}{2u+\lambda} \right) \quad (\text{A.9})$$

The interaction portion of this energy can be rewritten as

$$E_{\text{int}} = -\frac{\Omega^2}{d} \int \sum_j \frac{F_j^{(1)}(\underline{q})F_j^{(2)}(-\underline{q})}{c_j^2(0)q^2} \cos(\underline{q} \cdot \underline{R}) d^3q \quad (\text{A.10})$$

where $c_j(0)$ is the (isotropic) sound velocity at $q = 0$.

We note that (A.10) is the same as (A.5) except for the presence of $c_j^2(0)q^2$ in the denominator in place of $\omega_j^2(q)$. We shall now show that, for large R , the main contribution to the integral in (A.5) comes from $q \approx 0$, so that, asymptotically, the two expressions for the elastic interaction energy are identical.

The integrand in (A.5) is a function only of the magnitude of q and the angle θ between \underline{q} and \underline{R} . It can be expanded in a Fourier series in θ , or in a power series of the form

$$\sum_j F_j^{(1)}(\underline{q})F_j^{(2)}(-\underline{q}) \cos(\underline{q} \cdot \underline{R}) = \sum_n (a_n(q) \cos^n \theta + b_n(q) \sin \theta \cos^n \theta) e^{iqR \cos \theta} \quad (\text{A.11})$$

so that (A.5) becomes

$$\begin{aligned} E_{\text{int}} &= -\frac{2\pi\Omega^2}{d} \iint \sum_n (a_n(q) \cos^n \theta + b_n(q) \sin \theta \cos^n \theta) e^{iqR \cos \theta} dq \, d\cos \theta \\ &= -\frac{2\pi\Omega^2}{d} \int_0^\infty \sum_n \left[\frac{a_n(q)}{(iR)^n} \frac{\partial^n}{\partial q^n} \left(\frac{\sin qR}{qR} \right) + \frac{2\pi b_n(q)}{(iR)^n} \frac{\partial^n}{\partial q^n} \left(1 + \frac{\partial^2}{\partial q^2} \right) J_0(qR) \right] dq \end{aligned} \quad (\text{A.12})$$

For large R , we find (12)

$$\int_0^\infty a_n(q) \frac{\partial^n}{\partial q^n} \left(\frac{\sin qR}{qR} \right) dq$$

$$\begin{aligned}
&= (-1)^n \frac{1}{R} \operatorname{Im} \int_{-\infty}^{\infty} \frac{d^n a_n(q)}{dq^n} q^{-1} H(q) e^{iqR} dq + \sum_k \left[\frac{d^{2k-1} a_n(q)}{dq^{2k-1}} \frac{\partial^{n-2k}}{\partial q^{n-2k}} \left(\frac{\sin qR}{qR} \right) \right]_{q=0} \\
&= (-1)^n \frac{\pi}{2R} \frac{d^n a_n}{dq^n} \Big|_{q=0} + 0 \left(\frac{1}{R^2} \right) + \sum_k \left[\frac{d^{2k-1} a_n(q)}{dq^{2k-1}} \frac{\partial^{n-2k}}{\partial q^{n-2k}} \left(\frac{\sin qR}{qR} \right) \right]_{q=0}
\end{aligned} \tag{A.13}$$

where $H(q)$ is the Heaviside function

$$H(q) = \begin{cases} 0 & q < 0 \\ 1 & q \geq 0 \end{cases} \tag{A.14}$$

Similarly, for $m = n$ or $n + 2$ (cf. Eq. (A.12))

$$\begin{aligned}
&\int_0^{\infty} b_n(q) \frac{\partial^m}{\partial q^m} J_0(qR) dq \\
&\approx (-1)^n \int_0^{\infty} \frac{d^m b_n(q)}{dq^m} \sqrt{\frac{2}{\pi qR}} \cos(qR - \frac{\pi}{4}) dq + \sum_k \left[\frac{d^{2k-1} b_n(q)}{dq^{2k-1}} \frac{\partial^{m-2k}}{\partial q^{m-2k}} J_0(qR) \right]_{q=0} \\
&= (-1)^n \sqrt{\frac{2}{\pi R}} \operatorname{Re} \left\{ e^{-\frac{i\pi}{4}} \int_{-\infty}^{\infty} \frac{d^m b_n(q)}{dq^m} q^{-\frac{1}{2}} H(q) e^{iqR} dq \right\} + \sum_k \left[\frac{d^{2k-1} b_n(q)}{dq^{2k-1}} \frac{\partial^{m-2k}}{\partial q^{m-2k}} J_0(qR) \right]_{q=0} \\
&= (-1)^n \sqrt{\frac{2}{R}} \frac{d^m b_n}{dq^m} \Big|_{q=0} + 0 \left(\frac{1}{R^2} \right) + \sum_k \left[\frac{d^{2k-1} b_n(q)}{dq^{2k-1}} \frac{\partial^{m-2k}}{\partial q^{m-2k}} J_0(qR) \right]_{q=0}
\end{aligned} \tag{A.15}$$

Thus the main contribution to the integral in (A.5) comes from $q \approx 0$, which is what we wanted to prove.

This establishes the identity of the classical and quantum mechanical result.

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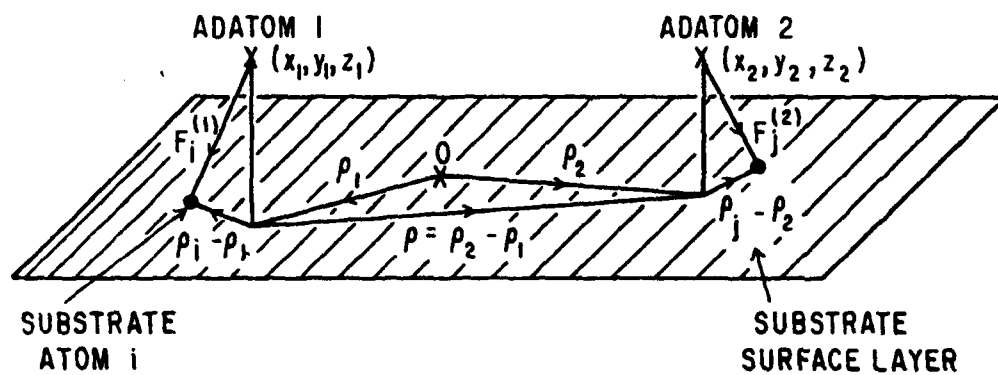


Fig 1

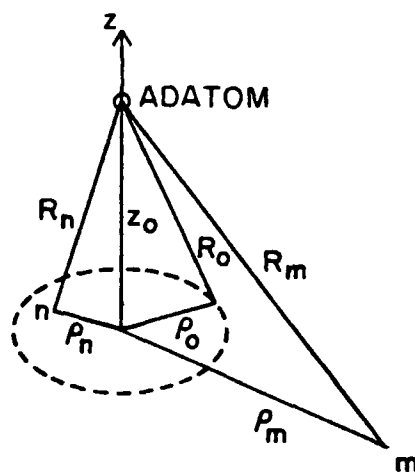


Fig 2

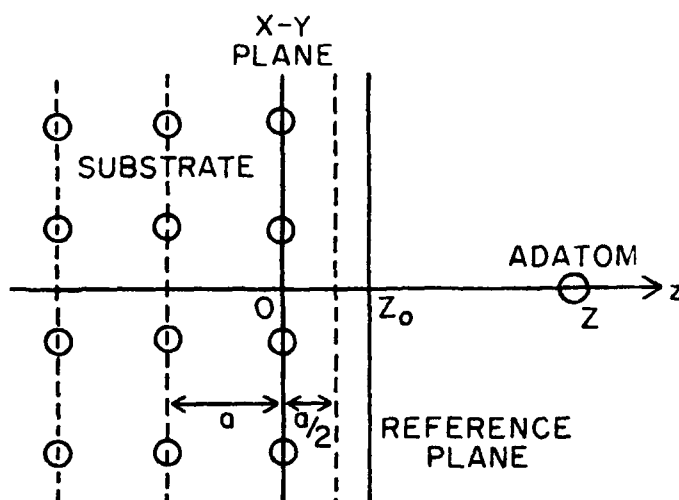


Fig. 3

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